

Surface and Adhesion Properties of Poly(ethylene glycol) on Polyester(polyethylene terephthalate) Fabric Surface: Effect of Air-Atmospheric Plasma Treatment

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ABSTRACT: The surface and adhesion properties of different molecular weight poly(ethylene glycol) (PEG) (400, 1500, and 3000 g/mol) on untreated and air-atmospheric plasma-treated PET woven fabrics were studied, with the aim of developing durable hydrophilic PET fibrous structures. PEG application was carried out by padding of the PET fabric in aqueous solution of PEG followed by curing and drying. The surface properties of the PEG-coated PET fabrics were then characterized using wicking test to measure the water contact angle (θ°) and capillary weight (W_c), and using atomic force microscopy (AFM) images in the tapping mode. Results showed that without a prior air-atmospheric plasma treatment of the PET fabric, the water contact angle decreased and capillary weight increased with the three PEGs, implying an increase in the hydrophilicity of both inner and outer PET fabric fiber

surface. Air-plasma treatment of the PET fabrics before PEG coating increases further the hydrophilicity of the inner fabric fiber surface: the capillary weight was almost doubled in the case of the three PEGs. Best results were obtained with PEG 1500: water contact angle decreasing from 82° to 51° , and the capillary weight increasing from 11 mg to 134 mg. Moreover, wash fastness test at room temperature and at 80°C confirms improved adhesion of PEG-1500 to the plasma-treated PET woven fabric surface, while under the same conditions the plasma-treated PET without PEG loses completely its hydrophilic character. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2621–2629, 2011

Key words: air-atmospheric plasma treatment; polyester fabric; polyethylene glycol; contact angle; capillarity; adhesion

INTRODUCTION

Polyester fabrics made from PET [poly(ethylene terephthalate)] accounts for almost 50% of all fiber materials. PET fibers have high uniformity, mechanical strength or resistance against chemicals or abrasion. However, high hydrophobicity, the build-up of static charges, stain retention during laundering and being difficult to finish are undesirable properties of PET.

Enhancement of the hydrophilicity of PET fibers is a key requirement for many applications, ranging from textile production to applications in the biomedical field.

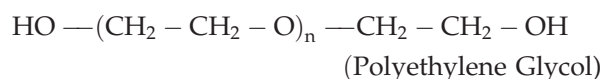
In the textile field, increased hydrophilic properties improves comfort in wear with a better moisture management due to increased wettability and wicking, but it also improves adhesion to other materials (coating for example), and dyeing.¹ Even soil-release properties of PET fabrics can be increased by increasing the PET surface hydrophilicity.²

Several strategies can be adopted to increase the surface energy and hence the hydrophilicity of PET fibers: by chemical finishing or grafting, or chemical surface treatment with NaOH^{3,4} or by a physical surface treatment using plasma or a biochemical treatment with enzymes.⁵

Although air-atmospheric plasma treatment is more environmentally friendly than NaOH treatment which causes drastic weight and strength losses,³ we showed in a previous article that the ageing with time causes loss of hydrophilic species formed by plasma treatment.⁶ Immobilizing a hydrophilic oligomer like PEG immediately after plasma treatment would perhaps yield a more durable hydrophilic treatment.

PEG can be used for surface modification because of its unique properties such as hydrophilicity, flexibility, and nontoxicity.⁷

It is a neutral polyether available in a variety of molecular weights. It is a water-soluble amphiphilic molecule, also soluble in most organic solvents. In aqueous solution PEG acts as a highly mobile molecule with a large exclusion volume.



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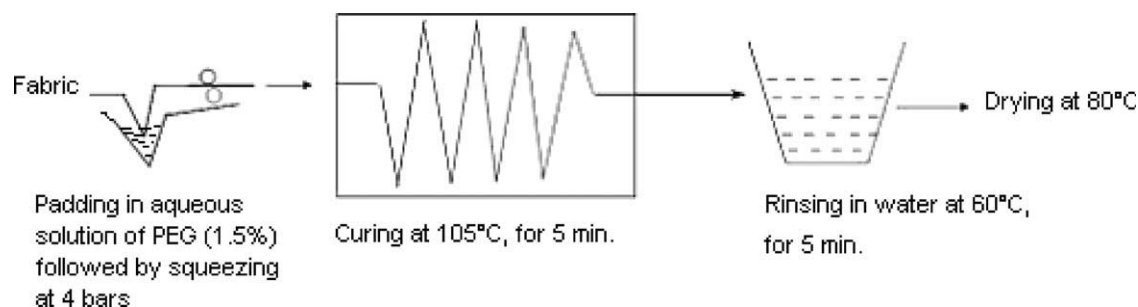


Figure 1 Application procedure of PEG on PET fabric by padding, squeezing followed by curing and a final rinsing before drying.

PEG has already been used to impart for example soil-release properties to polyester fibers in the form of a copolymer with blocks of polyethylene terephthalate and polyoxyethylene terephthalate that provide a structure that has regions of hydrophilicity interspersed with hydrophobic regions that have a strong attraction for the polyester surface.⁸

Different research methods have been used to bind PEG to various materials: from simple physical adsorption to chemical bond formation, such as chemical coupling and graft polymerization.^{7–10}

Various plasma treatment methods: argon-plasma treatment, oxygen-plasma treatment, radio frequency (RF) plasma polymerization, and atmospheric pressure glow discharge methods have been used to immobilize PEG molecules on polymer films and membranes.^{11–16} Moreover, several PEG application methods have been used for grafting of PEG to PET membranes using plasma treatment:

- Grafting PEG to a PET membrane surface functionalized with silicon tetrachloride (SiCl_4) plasma.¹¹
- Plasma treatment of PET membranes precoated with PEG using argon-plasma discharge treatment. Different molecular weight of PEG were thus immobilized on PET membrane by Wang et al.¹⁵
- Polymerizing gaseous PEG onto PET membrane using RF plasma polymerization of PEG.¹⁶

In the textile sector, where emphasis is being put on use of best available technologies¹⁷ to reduce environmental impact, air-atmospheric plasma treatment presents a definite advantage. It is cheap and can be used at high treatment speeds compared with low pressure plasma treatment employing oxygenated or inert gases which require high-cost vacuum equipment and high energy consumption.^{18–21}

Air-atmospheric plasma treatment,²¹ which uses a dielectric barrier discharge (DBD) does not require a vacuum system and can treat fibrous materials continuously meeting thus, the needs of on-line treatment of textile fabrics. Also, in our previous works, we already showed that air-atmospheric plasma suc-

cessfully treated fibrous PET structures though these differ to some extent from that of PET membrane because of their known porosity and air permeability.²¹ Thus, in our study, we chose to activate the PET fabrics with atmospheric plasma treatment before immobilizing PEG on the polyester fabric surface by padding.

Different molecular weight PEGs were used. Surface characterization methods, including wicking test which is different from that used for membranes, were carried out to evaluate the surface properties of the PEG treated PET fabrics. In addition, AFM imaging in the tapping mode and adhesion assessment of the PEG to PET fabric were realized using wash fastness test.

EXPERIMENTAL: SAMPLES AND METHODS

Sample preparation: PEG coating application and plasma treatment

A 100% polyester (PET) woven fabric of density 284 g/m^2 with a thickness of 0.56 mm and 63.5% porosity was used for the study. The PET woven fabric was cleaned with hot water at 80°C to be freed from surface impurities and spinning oil. The cleanliness of the PET samples was checked by measuring the surface tension of final rinsing water (used to clean the PET samples), which remained constant and equal to 72.6 mN/m that is the surface tension of pure water.

Immobilizing PEG using padding

Different molecular weights PEG 400, 1500, and 3000 from Fluka chemicals were immobilized on cleaned-untreated PET fabrics as well as plasma-treated PET fabric samples using padding and curing method.

For the padding process, the open-width PET fabric (untreated and plasma-treated one) was passed through an aqueous solution of PEG in water, followed by squeezing through two rollers (see Fig. 1).

At a squeezing pressure of four bars, the weight pick up remained almost constant around 56%. For

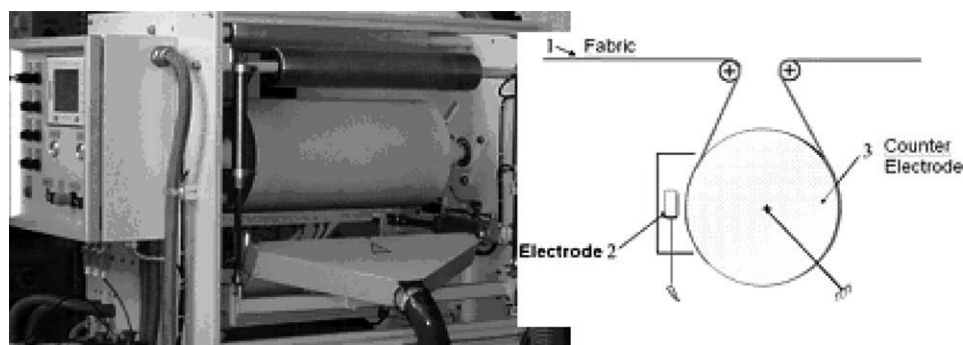


Figure 2 Plasma treatment under atmospheric pressure by means of dielectric barrier discharge, using "Coating Star" plasma machine manufactured by the Ahlbrandt System Company.

our experiment a "2 padding passages" was chosen as PEG application parameter. The other application conditions of the PEG coating on the PET fabric surface: PEG concentration, PEG curing temperature, and rinsing conditions, were varied to obtain increased hydrophilicity. Details are described in the Results section.

Plasma treatment of PET fabric

The PET woven fabric was cut into squared pieces of 50 cm × 50 cm on the basis of the electrode length of the plasma machine-50 cm (already described in a previous article)⁶.

Plasma treatment was carried out before PEG application, using an atmospheric plasma machine called "Coating Star" manufactured by Ahlbrandt System (Germany), see Figure 2.

The outer layer surfaces of both electrodes are of ceramic (a dielectric material), so that when these electrodes are subjected to a potential difference, a glow discharge called the DBD is created.

Atmospheric air was chosen as the gas during the atmospheric plasma treatments. The textile samples were indeed subjected to a treatment power (TP) of 60 kJ/m², which is the plasma power applied per m² of textile sample, expressed in kJ/m², and which is related to the velocity of the treatment (*V*) and the electrical power (*P*) of the machine, by the eq. (1):

$$TP = \left(\frac{P}{V \times L} \right) \times 0.06 \quad (1)$$

with

- P* = Electrical power (W)
- V* = Velocity of the sample (m/min)
- L* = Electrode length (m)
- TP = Treatment power (kJ/m²)

The following machine parameters were kept constant: frequency of 26 kHz, electrode length of

0.5 m and interelectrode distance of 1.5 mm. Plasma TP of samples was 1000 W and a speed of 2 m per min was used. After plasma treatment at 60 kJ/m², the plasma-treated samples were separated and packed in aluminum foil for further use.

Testing methods

Contact angle and capillary measurements using wicking test

To quantify the surface treatment modifications, contact angle as well as capillarity measurements were carried out on a tensiometer, 3S Balance from GBX Instruments (France). The apparatus mainly consists of an electronic microbalance with an accuracy of 0.1 mg, a mobile stage which can move vertically, and a data acquisition computer.

During measurements, a rectangular-shaped fabric sample of size "3 cm × 5 cm" was connected to the tensiometer at the weighing position, and its weight zeroed, and then it was progressively brought into contact with the surface of a liquid placed in a container on the mobile stage [see Fig. 3(a)]. The movement of the mobile stage was stopped when a sudden increase in weight was detected, which corresponded to a liquid meniscus formation on the fabric surface (*W_m*). A continuous increase of weight with time was recorded owing to liquid flow inside the fabric structure by capillarity, and the total wetting force (*W_t*) was recorded. At the end of the measurement, *t* = *t_{end}*, the fabric sample was separated from the liquid surface, and the weight of the liquid entrapped inside the fabric structure by capillarity [*W_c(t_{end})*] read directly on the screen of the balance.

Capillary weight [*W_c(t_{end})*] readings obtained are used for calculation of meniscus weight (*W_m*) of the fabric sample by using eq. (2).

$$W_m = W_t(t_{end}) - W_c(t_{end}) \quad (2)$$

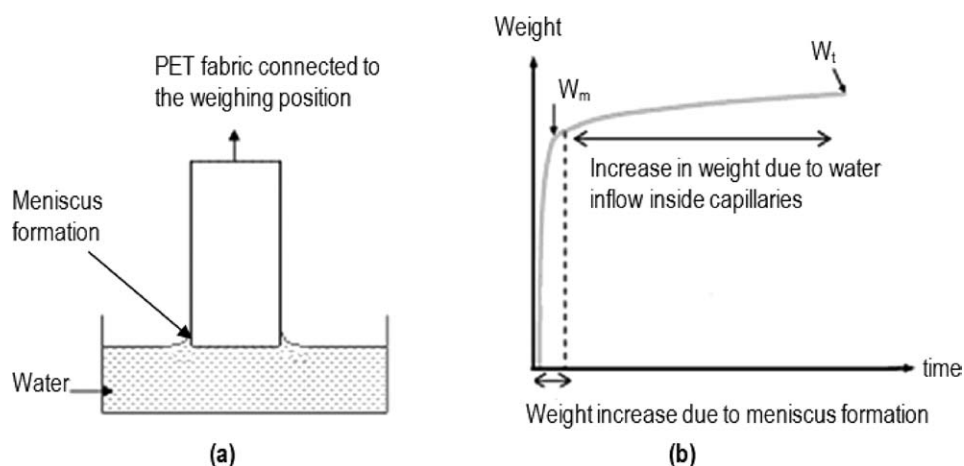


Figure 3 (a) Wettability and wicking tests using a tensiometer from GBX instruments, and (b) Typical trace of wetting and wicking curve displayed when the weight recorded is plotted against time.

where

W_m = Calculated meniscus weight (g)

W_t = Total weight at the end (g)

W_c = Capillarity weight at the end (g)

In all the experiments, $t_{\text{end}} = 3$ min.

Water contact angle calculations

The water contact angle at the woven sample surface could be determined from the calculated "meniscus weight" (W_m) using eq. (3),²¹ since both the surface tension of liquid water and the perimeter of the contacting surfaces were known.

$$W_m \times g = \gamma_L \times \cos\theta \times p \quad (3)$$

with

p = sample perimeter in contact with the liquid (mm)

W_m = Calculated meniscus weight (g)

$g = 9.81 \text{ g s}^{-2}$

γ_L = surface tension of the liquid (mN/m)

θ = contact angle ($^\circ$)

On average, five different samples were tested and their contact angle and capillary weight at 3 min measured.

AFM tapping mode images

Investigation using a "Nanoscope III" from DIGITAL INSTRUMENT was carried out for atomic force microscopy (AFM) imaging in the Tapping mode. Tapping mode tips "Budget sensor" from "Nanoandmore," of length 125 μm , made of monolithic

Silicon probe with aluminum coating and with resonance frequency of 300 kHz were used.

Tapping mode AFM imaging technique was carried out in ambient air to obtain topographic images of the PET fiber surface samples. This mode was preferred to the AFM/LFM (contact mode AFM), since the Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces which may arise after a plasma treatment, and which would distort image data.^{22,23}

The software also calculates the fiber surface roughness: R_a directly from AFM signals.

AFM imaging was carried out on five different fiber selected from each fabric sample, and in results part, only typical topographical images are presented.

Treatment durability-wash fastness test

The durability of the PEG treatment which was assessed using wash fastness test was carried out at room temperature and pressure (RTP) using pure water without soap or detergent. To test the wash fastness of the treated textile materials, a rectangular piece 2 cm \times 2 cm of each treated sample was subjected to four successive washing cycles of 5 min each by soaking in 20 mL of pure water (surface tension of 72.6 mN/m) at room temperature. The contact angle and capillary weight of the treated samples were monitored before and after wash fastness tests.

Further durability test consisted in assessing wash fastness at 80 $^\circ\text{C}$ using pure water (surface tension of 72.6 mN/m). Indeed the rectangular piece of each treated sample was subjected to washing cycles of 5 min each at 80 $^\circ\text{C}$ in the WASHTECH machine. The contact angle and capillary weight of the treated samples were monitored after each washing cycle.

RESULTS

Wetting and wicking test results on PEG immobilized on PET sample

In this part of study, the effect of immobilizing various weight PEGs (400, 1500, and 3000 g/mol) on cleaned-untreated and plasma-treated PET woven fabric was studied, using water contact angle and capillary weight measurements. The cleaned-untreated and plasma-treated PET fabric samples were padded in a 1.5% of PEG solution and then, cured at 105°C for 5 min followed by rinsing (to remove unfixed PEG) at 60°C in water for 5 min before a final drying at 80°C.

Effect of immobilizing PEGs on untreated PET fabric samples

Effect of the PEG nature. Results in Figure 4 show that the average water contact angle of cleaned-untreated PET-polyester fabric " $\theta = 82^\circ$ " is reduced to around 59°, 51°, and 52° respectively, when PEG 400, 1500, and 3000 are immobilized at the cleaned PET fabric surface. The average capillary weight value of the PET-polyester fabric increased from 11 mg to 32, 94, and 48 mg, respectively, for the PEG 400, 1500, and 3000.

The increase in PET fabric surface wettability by adsorption of PEG is due to the hydrophilic properties of the PEG molecules themselves. Immobilizing PEGs onto cleaned PET surface increases hydrophilicity of the cleaned polyester fabric both at the outer fabric fiber surface (lower contact angle) and the inner fabric fiber surface (higher capillary weight). This means that the PEGs are adsorbed both at the outer fabric fiber surface and at the inner fabric fiber surface inside the porous fabric structure. Best results in terms of increased capillarity and decreased contact angle is obtained with PEG 1500.

Effect of the PEG 1500 concentration and PEG 1500 curing temperature on surface properties of the PET fabrics. Two different concentrations of PEG-1500 aqueous solution were used, 1.5 and 2%, to coat the polyester fabric samples. Increasing PEG concentration from 1.5 to 2% did not increase the hydrophilicity of samples: the average water contact angle as well as capillary weight were 51° and 94 mg, respectively, at both PEG concentrations.

The effect of PEG-1500 curing temperature on the wettability results was then studied at three different curing temperatures 105, 120, and 135°C. The average water contact angle of the PEG coated PET fabric samples was the same: 51° for the three different curing temperatures, but the highest capillary weight value was obtained at 105°C— $W_c = 94$ mg instead of 78–81 mg at higher temperatures (120°C and 135°C respectively).

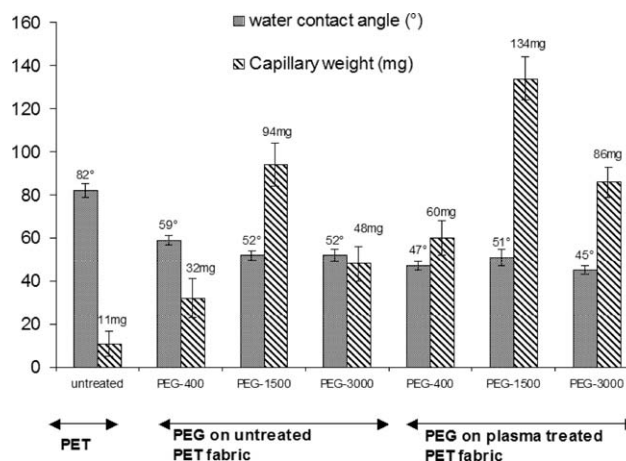


Figure 4 Effect of coating untreated and plasma-treated PET with different molecular weight PEG (400, 1500, and 3000 g/mol) on the fabric water contact angle and capillary weight.

Finally to obtain best hydrophilicity, PEG-1500 concentration and curing temperature were maintained at 1.5% and 105°C, respectively.

Effect of plasma treatment of PET samples before PEG application

Plasma treatment of the PET fabric before PEG application does have an impact on the wettability results, compared with previous results (see Fig. 4). For PEG 1500 and PEG 3000, though the average water contact angle of the fabrics does not vary a lot (46–51°), a significant slight decrease in water contact angle is observed in the case of PEG-400 (from 59° to 47°). In the case of the three PEGs, the average capillary weight is almost doubled when the PET fabric is plasma treated before PEG adsorption. The capillary weight increases from 32 to 60 mg for PEG 400; from 94 to 134 mg for PEG 1500, and from 48 to 86 mg for the PEG 3000. Highest capillary weight value is obtained when PEG 1500 is immobilized on the plasma-treated PET fabric.

Study of PEG adhesion on PET using wash fastness test

Influence of plasma treatment

To study the impact of plasma treatment on the adhesion of PEG-1500 to PET fabric, the coated fabrics were subjected to four successive washing cycles of 5 min each, at RTP. Contact angle and capillary weight were measured after each washing cycle. Results (Fig. 5) show that the number of washing cycles does not affect the water contact angle and capillary weight of the PEG-1500 immobilized on the plasma-treated PET fabric. However, in the case of the PEG-1500 immobilized on the untreated PET

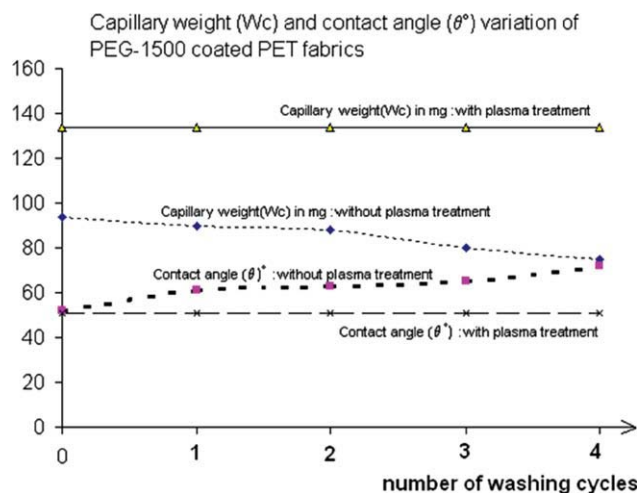


Figure 5 Variation in average capillary weight and contact angle with increasing washing cycles (1 cycle = 5 min) in distilled water at RTP, of the PEG-1500 coated untreated and plasma-treated PET fabric [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

fabric, the capillary uptake decreased and the water contact angle increased with increasing washing cycles, leading to a higher average water contact angle (70°) after four washing cycles. Indeed, in absence of a plasma treatment the surface adsorbed hydrophilic PEG molecules are easily washed out.

Influence of washing temperature on the adhesion of PEG to plasma-treated PET fabric

To study the influence of washing temperature on the adhesion of PEG-1500 to plasma-treated PET fabric, washing test was carried out at harsher condition 80°C. Moreover, to check that there was no more unfixed PEG at the PET surface after each washing cycle, the washed sample was further soaked in 20 mL of pure water at RTP: any loss of unfixed species lead to a decrease in the water surface tension.

Table I shows the average contact angle and capillary weight of PEG-1500 coated plasma-treated PET fabrics having been subjected to different washing cycles at 80°C.

Washing cycles decreased very slightly the water contact angle of the PEG coated plasma-treated PET fabric surface. The more or less constant water contact angle value (47–50°) shows that PEG molecules are still attached to the plasma-treated PET fiber surface and cannot be removed even under harsh conditions (80°C during 30 min). However, washing time did have an effect on the capillary weight which increased slowly and became stable after 30 min. Most probably, washing in harsh conditions removed free PEG molecules which blocked the capillary pores of the fabric inner structure, and this results in a higher water uptake by capillarity (wicking). Indeed complete removal of unlinked (free) PEG was achieved when the surface tension of the rinsing water was almost that of pure water ($\gamma = 72.6$ mN/m), that is, six washing cycles at 80°C was sufficient for complete removal of free PEG (see Table I).

AFM (tapping mode imaging)

Atomic force microscopy, in the tapping mode was carried out to better understand the different morphological changes occurring at the PET fabric fiber surface before and after PEG-1500 immobilization with and without a prior plasma treatment of the PET fabric surface.

Figure 6(a,b) show typical topographical images of a cleaned-untreated PET fiber with and without PEG coating, respectively. Although the surface roughness of the PET surface with or without PEG coating is almost the same (~70 nm), the untreated PET fiber seem quite smooth and homogeneous. However, after application of PEG, many small thin elliptical and irregular shaped deposits, most probably due to PEG, appear at the fiber surface [see Fig. 6(b)].

TABLE I
Effect of Varying Washing Time (at 80°C), on Average Capillary Weight and Contact Angle of PEG-1500 Coated Plasma Treated PET Fabric and on the Surface Tension of Water After Wash Fastness Test

Number of washing cycles of 5 min (at 80°C)	Average PET fabric water contact angle (°)	Average PET fabric capillary weight (mg)	Surface tension of water (mN/m) in which fabric sample was dipped for 1 minute at RTP, after the washing test at 80°C
1	51	134	64.2
2	47	153	67.3
3	47	149	69.4
4	47	160	71.0
5	46	161	71.9

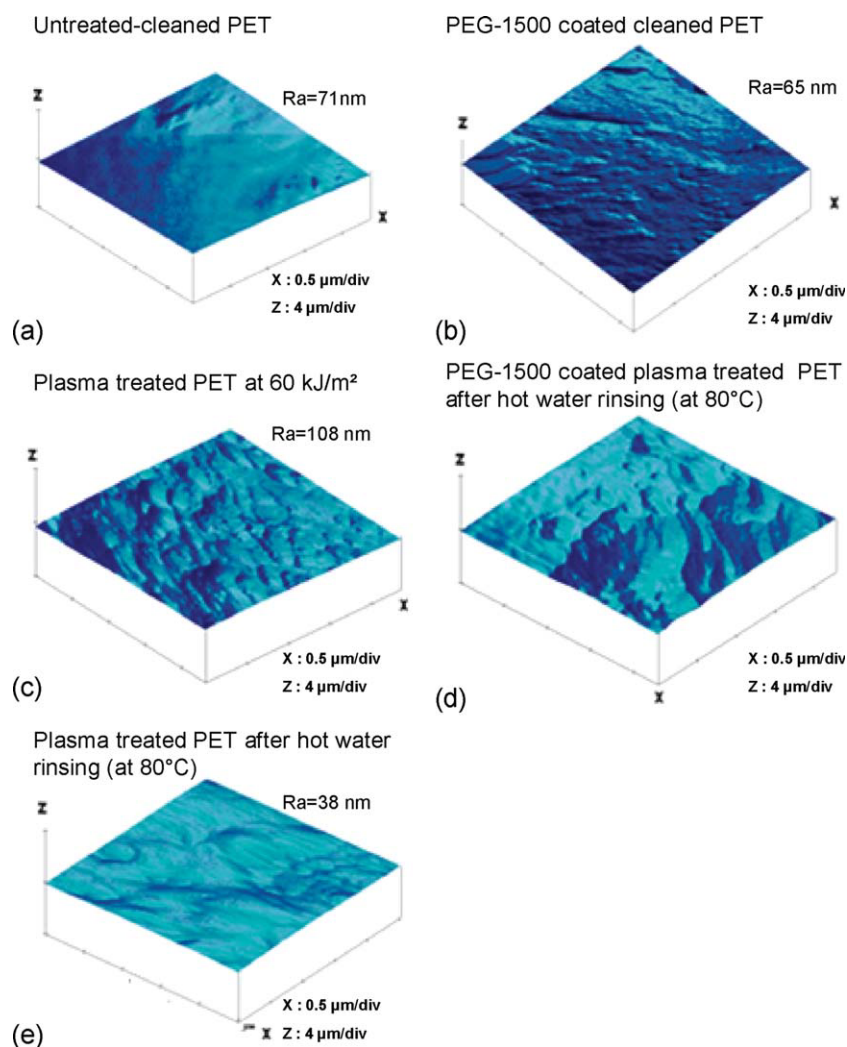


Figure 6 Tapping Mode AFM Topographical images of (a) an untreated PET fiber, (b) a PEG-1500 coated untreated PET fiber, (c) a plasma-treated PET fiber at 60 kJ/m^2 , (d) a PEG-1500 coated plasma-treated PET fiber after wash fastness test at 80°C, (e) a plasma-treated PET fiber after a wash fastness test at 80°C [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

Figure 6(c) shows a typical topographical image of plasma-treated PET fiber (at 60 kJ/m^2) without PEG coating. Uniform scale-shaped bumps can be seen on the overall plasma-treated PET fiber surface [see Fig. 6(c)] which has a higher surface roughness ($R_a = 108 \text{ nm}$) than the untreated PET fiber ($R_a = 70 \text{ nm}$): there are nearly six such scale shaped bumps per μm in the x-direction. These scales would appear as a result of PET fiber surface etching caused by plasma treatment.

Figure 6(d) shows the topographical image of the PET fiber surface after the plasma treatment followed by PEG coating and a wash fastness treatment at 80°C during 30 min. In certain regions [$x = 1\text{--}2 \mu\text{m}$, see Fig. 6(d)], the PEG appears in the foreground relief as big bumps covering the regular scaly shaped bumps which can no longer be perceived. However, on the upper part of the image

($x = 0\text{--}1$), the scaly shaped bumps still appear as if the gaps (valleys) in between scales have not been completely filled with PEG in that region, most probably, because either the PEG does not cover them at all, or only a thin layer of PEG covers the scaly bumps. Indeed, surface analysis of plasma-treated PET without PEG coating and having been subjected to the same wash fastness test (80°C), shows complete disappearance of the scaly shaped PET surface [see Fig. 6(e)]: only traces or finger prints of the scales appear leaving a smooth surface ($R_a = 38 \text{ nm}$). This means that most probably, the PEG coating does cover all the bumped scaly surfaces formed as a result of plasma treatment, and that is why, even after the wash fastness test at 80°C, the scaly shaped bumps still appear on the topographical image of the PEG coated plasma-treated PET fabric [Fig. 6(d)].

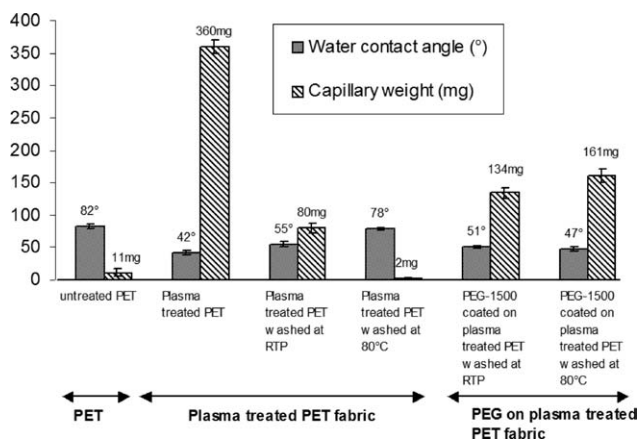


Figure 7 Comparing the effect of different treatment (plasma and/or PEG coating) and wash fastness test at RTP (room temperature and pressure) and at 80°C, on the water contact angle and the capillary weight of PET woven fabrics.

Comparison with plasma treatment alone

Plasma treatment alone increases the hydrophilicity of PET fabric, but the polar species formed are gradually lost during washing, even at RTP, yielding an increase in water contact angle from 42° to 55°, and a considerable decrease in capillary weight from 360 to 80 mg after 30 min (see Fig. 7). Under harsher conditions (washing at 80°C for 30 min), the wettability of the plasma-treated PET reaches that of untreated PET fabric (see Fig. 7) meaning that there is complete loss of all polar species, but also, the regular scaly bumps formed as a result of plasma treatment [Fig. 6(c)], disappear [see Fig. 6(e)]. However, application of PEG on a plasma-treated PET cover the scaly bumps, and strong bonding takes place between the PEG and the polar species at plasma-treated PET surface preventing their removal even under harsh washing condition (80°C).

DISCUSSION

Different molecular weight PEGs (400, 1500, and 3000 g/mol) may be easily immobilized on a PET woven fabric by padding and curing process, increasing thus the hydrophilicity of the PET fabric both in terms of decreased water contact angle and increased capillary weight that is there is increased hydrophilicity both at the outer PET fabric surface and at the inner woven fabric fiber surface.

This increased hydrophilicity of the PET fabric is conferred by the PEG molecules adsorbed at the PET surface. Indeed, the PEG molecules have terminal diol character and polyether character along the chain favoring hydrogen bonding with water. The PET has however, no chemically active group capable of reacting with the —OH group of the PEG,

except a few end-terminal —COOH groups, capable of forming hydrogen bonds with the —OH (end-terminal group) or ether groups of the PEG. It is also probable that covalent bonds may be formed between the —COOH of PET and the —OH (end-terminal group) of the PEG.

Air-atmospheric plasma treatment of the PET fabric before PEG application increases further the hydrophilicity of the PEG coated PET fabrics, especially in terms of increased capillary weight. The average water contact angles are similar for the three PEGs and are in-line with those obtained by Wang¹⁵ with PET membranes. Compared with untreated fabrics, the average capillary weight is nearly doubled in the case of the three PEGs. Best results are obtained with the PEG 1500. Moreover, there is also an increased adhesion between the PEG 1500 and the PET fabric. Indeed, with plasma treatment, chain-scissions of the PET create polar carbonyl, carboxyl, and hydroxyl groups,^{24–26} and at a TP of 60 KJ/m², an increase in the n(O)/n(C) ratio from 33 to 66% was measured by X-ray photoelectron spectroscopy (XPS) as described in our previous work.²⁰ The increased adhesion between plasma-treated PET and the PEG 1500 can be explained by a greater quantity of polar groups at the PET surface which increase hydrogen bonding between the PEG 1500 and PET fabric.

Indeed with long chain molecules such as PEG 1500, segments of the chain may physi-sorb onto PET surface with the formation of adsorbed loops of PEG 1500 on the PET just like adsorbed polymer chain which consist of sequences and loops²⁷: this would give rise to multiple point bonding between a PEG molecule and the PET surface. While with the untreated PET only weak bond “Van der Waals” forces may be predominantly present at these multiple point bondings, in the case of plasma treatment, multiple hydrogen bonding may take place between the ether groups of the PEG and the newly plasma created terminal —COOH groups of the PET.

With the smaller chain PEG 400, it is most probable that the PEG adopts a brush conformation (instead of loops) at the PET surface,²⁸ with only one of the end-terminal OH of the PEG interacting with free —COOH of PET. The capillary weight for PEG 400 does not however reach that of PEG 1500. It may be because the brush conformation reduces capillary pore diameters and so water uptake is reduced.

For the higher molecular weight PEG 3000, the smaller capillary weight ($W_c = 48$ mg) compared with the PEG 1500 could be due to the steric hindrance conferred by larger PEG 3000 molecules immobilized at the inner fabric fiber surface, which lowers down the rate of water up-flow through the capillary structure formed by the polyester fabric pores.

With the PEG 1500 applied after surface activation with plasma, increase of capillary weight after

washing at 80°C would mean that any pendant non fixed PEG molecule blocking capillary pores is removed.

The great discrepancy in the water contact angle measured for the PEG 400 without and with a prior plasma treatment may be explained by the extent of PET surface coverage by the PEG 400 brushes. For the untreated PET, as the number of free —COOH group is low, fewer PEG 400 brushes are fixed by hydrogen bonding to the PET surface, but after plasma treatment as the number of —COOH increases, there is a better coverage of the PET by this PEG 400, leading to a smaller water contact angle (47° instead of 59°). Surface coverage of the untreated PET by the longer PEG 1500 is better because of the possibility of loop formation and multipoint bonding weak bondings (Van der Waal or Hydrogen bonds).

Capillary values are in general higher after plasma treatment for all PEGs because of higher capillarity flow of the PEGs into pores with higher surface energy capillary walls.

Although plasma treatment alone does provide a way of increasing to a large extent the hydrophilicity of the PET fabric surface, it degrades not only with time and UV exposure time (as described in our previous article⁶) but also with washing time at RTP, and high temperature treatment (80°C) in aqueous conditions degrades totally the plasma-treated surface. Plasma treatment however improves adhesion between PEG and the PET fabric surface. Although the hydrophilicity reached with the combination of both plasma and PEG is lower than plasma treatment alone, it is nevertheless more permanent.

CONCLUSIONS

Our work highlights the beneficial effect of a prior treatment of the PET fabric using air-atmospheric plasma for a more permanent hydrophilic functionalization of polyester fabrics with PEG. Indeed padding with PEG alone (without plasma treatment) increases the hydrophilicity of PET and water contact angle decrease is dependent on the molecular weight of the PEG used (PEG 1500 yielding lowest water contact angle). However, all the PEGs are easily washed off from the PET fabric surface without a prior plasma treatment.

Although the hydrophilic character conferred to PET fabrics by air-atmospheric plasma treatment alone is not permanent, it improves the adhesion between the PEG and the plasma-treated PET fabric.

Using PEG 1500 and a PET surface preactivated by air-atmospheric plasma, it is possible to add to all the advantages of increased hydrophilicity (increased comfort, or soil-release properties), the beneficial effect of increased durability of the PEG

finishing to textile processing and after care (like washing or dyeing).

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